### **ENT COOPERATION TREATY**

## **PCT**

#### **INTERNATIONAL SEARCH REPORT**

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file ref rence FOR FURTHER see Notification of Transmittal of International Search R port			
243513-PCT	20) as well as, where applicable, item 5 below.		
International application No.	International filing date (day/month/year)	(Earliest) Priority Date (day/month/year)	
PCT/ZA 00/00024	11/02/2000	11/02/1999	
Applicant			
CTEINED Deiling Doniel			
STEINER, Philipp, Daniel			
This International Seamh Depost has been	n amount by this International Counting Aut	and in American the day the continues	
according to Article 18. A copy is being tra	n prepared by this International Searching Auth ansmitted to the International Bureau.	ionty and is transmitted to the applicant	
This lease where I Ocean Broad are size.	atamatat 3 stars		
This International Search Report consists  It is also accompanied by	of a total of3 sheets. a copy of each prior art document cited in this	report.	
Basis of the report  All the report to the lenguage the i			
language in which it was filed, unle	intemational search was carried out on the bas ess otherwise indicated under this item.	sis of the international application in the	
the international search was Authority (Rule 23.1(b)).	as carried out on the basis of a translation of the	ne international application furnished to this	
b. With regard to any nucleotide and		temational application, the international search	
was carried out on the basis of the contained in the internation	e sequence listing : nal application in written form.		
=	mational application in computer readable form	1.	
furnished subsequently to	this Authority in written form.		
furnished subsequently to	this Authority in computer readble form.		
the statement that the sub international application as	sequently fumished written sequence listing do s filed has been fumished.	pes not go beyond the disclosure in the	
the statement that the info furnished	rmation recorded in computer readable form is	identical to the written sequence listing has be n	
2. Certain claims were four	nd unsearchable (See Box I).		
3. Unity of invention is lack	dng (see Box II).		
4. With regard to the title,			
the text is approved as sul	bmitted by the applicant.		
	ned by this Authority to read as follows:		
_			
5. With regard to the abstract,			
The text is approved as submitted by the applicant.			
the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.			
6. The figure of the drawing to be public	,		
as suggested by th applic	•	X Non of the figures.	
because the applicant faile	ed to suggest a figure.	<del>_</del>	
because this figure better	charact riz s the invention.		

# A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07D307/50

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT			
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	
Α	DE 31 39 188 C (H. KNAUTH) 28 July 1983 (1983-07-28) claims 1,2	1-13	
A	WO 81 00407 A (BERTIN & CIE.) 19 February 1981 (1981-02-19) claims 1-30	1-13	
A	DE 38 42 825 A (FRIEDR. KRUPP GMBH) 20 July 1989 (1989-07-20) claims 1-10	1-13	
А	US 4 533 743 A (D. J. MEDEIROS, M. B. BURNETT) 6 August 1985 (1985-08-06) claims 1-13/	1-6	
	·		

X Further documents are listed in the continuation of box C.	γ Patent family members are listed in annex.
<ul> <li>Special categories of cited documents:</li> <li>"A" document defining the general state of the art which is not considered to be of particular relevance</li> <li>"E" earlier document but published on or after the international filling date</li> <li>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</li> <li>"O" document referring to an oral disclosure, use, exhibition or other means</li> <li>"P" document published prior to the international filing date but later than the priority date claimed</li> </ul>	<ul> <li>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</li> <li>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</li> <li>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</li> <li>"&amp;" document member of the same patent family</li> </ul>
Date of the actual completion of the international search	Date of mailing of the international search report
27 June 2000	06/07/2000
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  Fax: (+31-70) 340-3016	Herz, C

1

## INTERNA NAL SEARCH REPORT

		PC1/ZA 00,	7 00024
.(Continu	ation) DOCUMENTS CONSIDERED TO BE RELEVANT		
ategory °	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
A	EP 0 346 836 A (JEDNOTE ZEMEDELSKE DRUZSTVO JANA CERNEHO SE SIDLEM) 20 December 1989 (1989-12-20) claims 1-11		1-13
A	WO 96 25553 A (F + S MARKET, SPOL. S.R.O.) 22 August 1996 (1996-08-22) claims 1-14		1-13
A	US 4 029 515 A (K. KIMINKI ET AL.) 14 June 1977 (1977-06-14) claims 1-7		1-13
A	DATABASE WPI Week 8648 Derwent Publications Ltd., London, GB; AN 1986-317829 XP002141089 & SU 1 225 841 A (KRASD. POLY.), 23 April 1986 (1986-04-23) abstract		1-13

1

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Intermedial Application No
PCT/ZA 00/00024

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 3139188	С	28-07-1983	NONE	
WO 8100407	A	19-02-1981	FR 2462433 A BR 8008782 A DE 3068793 D EP 0033323 A HU 185421 B IN 153609 A JP 56501046 T SU 1176840 A US 4366322 A	13-02-1981 26-05-1981 06-09-1984 12-08-1981 28-02-1985 28-07-1984 30-07-1981 30-08-1985 28-12-1982
DE 3842825	A	20-07-1989	CH 678183 A FI 886014 A US 4912237 A ZA 8900080 A	15-08-1991 09-07-1989 27-03-1990 25-10-1989
US 4533743	Α	06-08-1985	NONE	
EP 346836	Α	20-12-1989	CS 8804060 A DK 289889 A FI 892888 A HU 50802 A	14-11-1990 14-12-1989 14-12-1989 28-03-1990
WO 9625553	Α	22-08-1996	CZ 9500320 A AU 4480596 A	14-08-1996 04-09-1996
US 4029515	A	14-06-1977	FI 291174 A CA 1051884 A CS 191945 B DD 124873 A DE 2541119 A FR 2286853 A HU 170628 B IT 1043052 B NO 753114 A,B SE 425508 B SE 7510297 A SU 652902 A	05-04-1976 03-04-1979 31-07-1979 16-03-1977 08-04-1976 30-04-1976 28-07-1977 20-02-1980 06-04-1976 04-10-1982 05-04-1976
SU 1225841		 23-04-1986	NONE	



## **PCT**

## **INTERNATIONAL PRELIMINARY EXAMINATION REPORT**

(PCT Article 36 and Rule 70)

Applicant's	or ag	ent's file reference	<del></del>		0 11-55-	
243513 FOR FURTHER A		CTION		ation of Transmittal of International  / Examination Report (Form PCT/IPEA/416)		
International application No. International filing date		day/month	/year)	Priority date (day/month/year)		
PCT/ZA	00/00	024	11/02/2000			11/02/1999
	International Patent Classification (IPC) or national classification and IPC C07D307/50					
Applicant						
STEINE	R, Ph	ilipp, Daniel et al.				
		ational preliminary exam smitted to the applicant a		prepared	by this Inte	ernational Preliminary Examining Authority
2. This	REPO	ORT consists of a total of	4 sheets, including this	s cover st	neet.	
b	een a		sis for this report and/or	sheets c	ontaining re	n, claims and/or drawings which have ctifications made before this Authority e PCT).
Thes	e ann	exes consist of a total of	sheets.			
3. This i	eport	contains indications rela	iting to the following iter	ns:		
i	Ø	Basis of the report				
u		Priority				
111				ovelty, inv	entive step	and industrial applicability
IV		Lack of unity of invention				
V	Ø	Reasoned statement un citations and explanation			novelty, inve	entive step or industrial applicability;
VI		Certain documents cite		3111011.		
VII		Certain defects in the in				
VIII	$\boxtimes$	Certain observations or		cation		
Date of sub	Date of submission of the demand			Date of c	ompletion of	this report
08/09/20	00			25.05.20	01	·
		address of the international	l	Authorize	ed officer	B NEO ES MIZUR
preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d			Herz, C		Same of the same o	
Fax: +49 89 2399 - 4465				Telephon	e No. +49 89	2399 8275

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/ZA00/00024

i.	Ba	sis of the report	
1.	the and	receiving Office in I	nents of the international application (Replacement sheets which have been furnished to response to an invitation under Article 14 are referred to in this report as "originally filed" this report since they do not contain amendments (Rules 70.16 and 70.17)):
	1-6	3	as originally filed
	Cla	aims, No.:	
	1-1	3	as originally filed
	Dra	awings, sheets:	
	1-2		as originally filed
	1-2	•	as originally med
2.		-	uage, all the elements marked above were available or furnished to this Authority in the nternational application was filed, unless otherwise indicated under this item.
	The	ese elements were a	vailable or furnished to this Authority in the following language: , which is:
		the language of a t	ranslation furnished for the purposes of the international search (under Rule 23.1(b)).
		the language of pu	blication of the international application (under Rule 48.3(b)).
		the language of a t 55.2 and/or 55.3).	ranslation furnished for the purposes of international preliminary examination (under Rule
3.		_	eotide and/or amino acid sequence disclosed in the international application, the examination was carried out on the basis of the sequence listing:
		contained in the int	ernational application in written form.
		filed together with t	he international application in computer readable form.
		furnished subseque	ently to this Authority in written form.
		furnished subseque	ently to this Authority in computer readable form.
			the subsequently furnished written sequence listing does not go beyond the disclosure in plication as filed has been furnished.
		The statement that listing has been fur	the information recorded in computer readable form is identical to the written sequence nished.
4.	The	e amendments have	resulted in the cancellation of:
		the description,	pages:
		the claims,	Nos.:

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/ZA00/00024

•		the drawings,	sheets:
5.			established as if (some of) the amendments had not been made, since they have been ond the disclosure as filed (Rule 70.2(c)):
		(Any replacement she report.)	eet containing such amendments must be referred to under item 1 and annexed to this
6.	Add	litional observations, if	necessary:

- V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- 1. Statement

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Novelty (N) Yes: Claims 1-13

No: Claims

Inventive step (IS) Yes: Claims 1-13

No: Claims

Industrial applicability (IA) Yes: Claims 1-13

No: Claims

2. Citations and explanations see separate sheet

#### VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made: see separate sheet

Due to the specific process steps and parameters the claimed process for the production of 1. furfural is considered to be novel vis-à-vis the state of the art as represented by the documents cited in the International Search Report.

Vis-à-vis this state of the art an inventive step can be acknowledged since, for the process claimed, the parameters and conditions as well as its yield in the order of 100% have not been obvious to a person skilled in the art.

2. The use of the terms "a... predetermined temperature" and "a gradual reduction of pressure" in Claim 1 without further definitive qualification therein renders this claim obscure in scope in that it does not indicate any specific values. The claims shall define the matter for which protection is sought and therefore the meaning of the terms of a claim should, as far as possible, be clear for the person skilled in the art and not throw doubt on the extent of protection (Article 6 PCT). However, the amendments to Claim 1 as proposed in Applicant's letter dated 13/03/01 could be regarded as sufficiently clear in defining the terms objected to.

## PF NT COOPERATION TREAT

From the	INTERN	ATIONAL	<b>BUREAU</b>
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### **PCT**

#### **NOTIFICATION OF ELECTION**

(PCT Rule 61.2)

То:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT

2011 South Clark Place Room

CP2/5C24 Arlinaton, VA 22202

ETATS-UNIS D'AMERIQUE  in its capacity as elected Office		
Applicant's or agent's file reference 243513-PCT		
Priority date (day/month/year) 11 February 1999 (11.02.99)		

	ZEITSCH, Karl, J.
1.	The designated Office is hereby notified of its election made:
	X in the demand filed with the International Preliminary Examining Authority on:
	08 September 2000 (08.09.00)
	in a notice effecting later election filed with the International Bureau on:
2.	The election X was
	was not
	made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

Authorized officer

Maria Kirchner

Telephone No.: (41-22) 338.83.38

Facsimile No.: (41-22) 740.14.35

## PATENT COOPERATION TREAT.

	From the INTERNATIONAL BUREAU			
PCT	То:			
NOTIFICATION OF THE RECORDING OF A CHANGE  (PCT Rule 92bis.1 and Administrative Instructions, Section 422)  Date of mailing (day/month/year) 14 August 2001 (14.08.01)	MORRISON, Ian Ian Morrison Forst_r & Company FMI House, Gleneagles Park Flanders Drive, Mount Edgecombe P.O. Box 2004 4300 Kwa Zulu Natal AFRIQUE DU SUD			
Applicant's or agent's file reference	IMPORTANT NOTIFICATION			
243513-PCT				
International application No. PCT/ZA00/00024	International filing date (day/month/year) 11 February 2000 (11.02.00)			
1. The following indications appeared on record concerning:				
X the applicant the inventor	the agent the common representative			
Name and Address STEINER, Philipp Daniel	State of Nationality State of Residence			
and ZEITSCH, Karl, J.	Telephone No.			
	Facsimile No.			
	Teleprinter No.			
2. The International Bureau hereby notifies the applicant that the	the following shangs has been recorded concerning:			
the person the name the add				
Name and Address	State of Nationality State of Residence			
INTERNATIONAL FURAN TECHNOLOGY	ZA ZA			
(PTY) LIMITED 5B New Era House	Telephone No.			
6 Joseph Avenue				
Glen Anil 4051 Kwa Zulu Natal South Africa	Facsimile No.			
	Teleprinter No.			
3. Further observations, if necessary: Assignement from the applicants in box 1 to the applicant in box 2. The applicants in box 1 remain as applicants for the US only.				
4. A copy of this notification has been sent to:				
X the receiving Office	the designated Offices concerned			
the International Searching Authority	X the elected Offices concerned			
the International Preliminary Examining Authority	other:			
	Authorized officer			
The International Bureau of WIPO				
34, chemin des Colombettes 1211 Geneva 20, Switzerland	V. Gross (Fax 338.87.40)			
Facs' No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38			

Form P./306 (March 1994)

004210365

## P/ NT COOPERATION TREAT

	From t	he INTERNATIONAL I	BUREAU
PCT	To:		
NOTIFICATION OF THE RECORDING OF A CHANGE  (PCT Rule 92bis.1 and Administrative Instructions, Section 422)  Date of mailing (day/month/year) 08 January 2001 (08.01.01)	lan FMI Flan P.O. 4300	RRISON, Ian Morrison Forster & Co House, Gleneagles Pa ders Drive, Mount Ed Box 2004 ) Kwa Zulu Natal IQUE DU SUD	ark
Applicant's or agent's file reference	<u> </u>	IMPORTANT NO	TIFICATION
243513-PCT	1		
International application No. PCT/ZA00/00024		ebruary 2000 (11.02.0	
1. The following indications appeared on record concerning:  X the applicant the inventor  Name and Address  STEINER, Philipp, Daniel Fleur de Lys Everton Road Kloof 3600 Zwa Zulu Natal	the age	State of Nationality ZA Telephone No.  Facsimile No.	State of Residence ZA
South Africa  2. The International Bureau hereby notifies the applicant that the second secon	the following	Teleprinter No.	concerning:
the person the name X the ad-	г	the nationality	the residence
Name and Address  STEINER, Philipp, Daniel Fleur de Lys Everton Road Kloof 3600 Kwa Zulu Natal South Africa		State of Nationality ZA Telephone No. Facsimile No. Teleprinter No.	State of Residence ZA
3. Further observations, if necessary:			
4. A copy of this notification has been sent to:			
X the receiving Office		the designated Offices	concerned
the International Searching Authority	֟֟֟֟	X the elected Offices con	cerned
X the International Preliminary Examining Authority	L	other:	
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized	Sean Taylor	
Facsimile No.: (41-22) 740.14.35	Telephone	No.: (41-22) 338.83.38	

### PCT

#### LD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



#### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7: C07D 307/50

A1

(11) International Publication Number:

(43) International Publication Date:

WO 00/47569

17 August 2000 (17.08.00)

(21) International Application Number:

PCT/ZA00/00024

(22) International Filing Date:

11 February 2000 (11.02.00)

(30) Priority Data:

199 05 655.2

11 February 1999 (11.02.99)

DE

(71) Applicant (for all designated States except US): STEINER, Philipp, Daniel [ZA/ZA]; Fleur de Lys, Everton Road, Kloof, 3600 Zwa Zulu Natal (ZA).

(72) Inventor; and

(75) Inventor/Applicant (for US only): ZEITSCH, Karl, J. [DE/DE]; Dürener Strasse 393, D-50935 Köln (DE).

(74) Agents: MORRISON, Ian et al.; Ian Morrison Forster & Company, FMI House, Gleneagles Park, Flanders Drive, Mount Edgecombe, P.O. Box 2004, 4300 Kwa Zulu Natal (ZA).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG. KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### **Published**

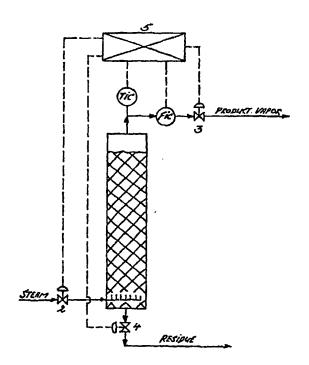
With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

#### (54) Title: PROCESS FOR THE MANUFACTURE OF FURFURAL

#### (57) Abstract

In a new process for the manufacture of furfural, a "pentosan-containing raw material acidified or not, is heated to a temperature T<sub>1</sub> by admitting steam through valve 2 while the valves 3 and 4 are closed. During the very short heating process, the steam condenses, thus increasing the moisture content of the charge. Then, valve 2 is closed and a leak valve 3 is opened so as to produce a steady small flow of product vapour by gradual depressurisation. This causes a slow drop in temperature. When in this fashion a suitably chosen temperature T<sub>2</sub> is reached, the leak valve 3 is closed to terminate the first "gradual depressurisation". If at the end of this period no more furfural was obtained, the digestion is completed by opening valve 4 to discharge the residue. If, however, furfural was still obtained, the reactor is reheated and submitted to another "gradual depressurisation" period.



Schematic of the delayed decompression process for the production of furfural.

## TENT COOPERATION TRE

**PCT** 

2Y			
REC'D	2 9	MAY	2001
WIPC	) }		PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference		
1	AR CHARTIER ARTICL	ee Notification of Transmittal of International reliminary Examination Report (Form PCT/IPEA/416)
	temational filing date (day/month/yea	ar) Priority date (day/month/year)
· · ·	1/02/2000	11/02/1999
International Patent Classification (IPC) or national		
C07D307/50		
Applicant		
STEINER, Philipp, Daniel et al.		
This international preliminary examinati and is transmitted to the applicant acco		this International Preliminary Examining Authority
2. This REPORT consists of a total of 4 s	heets, including this cover sheet	<u>.</u>
	, •	
		escription, claims and/or drawings which have
(see Rule 70.16 and Section 607 of		aining rectifications made before this Authority under the PCT).
These approves consist of a total of abo	a e te	
These annexes consist of a total of she	ets.	
	····	
3. This report contains indications relating	to the following items:	
I ⊠ Basis of the report		
II Priority		
III   Non-establishment of opinion	on with regard to novelty, inventi	ve step and industrial applicability
IV  Lack of unity of invention		
V 🖾 Reasoned statement under citations and explanations s		elty, inventive step or industrial applicability;
VI ☐ Certain documents cited		
VII	ational application	
VIII 🛛 Certain observations on the	international application	
Date of submission of the demand	Date of comp	oletion of this report
08/09/2000	25.05.2001	
Name and mailing address of the international	Authorized of	fficer
preliminary examining authority:		and the state of t
European Patent Office D-80298 Munich Tol. 40.80.2300 0. The E23656 com	Herz, C	
Tel. +49 89 2399 - 0 Tx: 523656 epm Fax: +49 89 2399 - 4465		0. +49 89 2399 8275

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/ZA00/00024

•			
<b>!</b> .	Ba	sis fth rprt	
1.	the and	receiving Office in re	ents of the international application (Replacement sheets which have been furnished to esponse to an invitation under Article 14 are referred to in this report as "originally filed" this report since they do not contain amendments (Rules 70.16 and 70.17)):
	1-6	;	as originally filed
	Cla	nims, No.:	
	1-1	3	as originally filed
	Dra	awings, sheets:	
	1-2	-	as originally filed
2.			rage, all the elements marked above were available or furnished to this Authority in the ternational application was filed, unless otherwise indicated under this item.
	The	ese elements were av	vailable or furnished to this Authority in the following language: , which is:
		the language of a tr	anslation furnished for the purposes of the international search (under Rule 23.1(b)).
		the language of pub	lication of the international application (under Rule 48.3(b)).
		the language of a tr 55.2 and/or 55.3).	anslation furnished for the purposes of international preliminary examination (under Rule
3.			eotide and/or amino acid sequence disclosed in the international application, the examination was carried out on the basis of the sequence listing:
		contained in the inte	rnational application in written form.
		filed together with th	e international application in computer readable form.
		furnished subseque	ntly to this Authority in written form.
		furnished subseque	ntly to this Authority in computer readable form.
			the subsequently furnished written sequence listing does not go beyond the disclosure in plication as filed has been furnished.
		The statement that the listing has been furn	the information recorded in computer readable form is identical to the written sequence ished.
١.	The	amendments have r	esulted in the cancellation of:
		the description,	pages:
		the claims,	Nos.:



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/ZA00/00024

•		the drawings,	sheets:		
5.		•		-	some of) the amendments had not been made, since they have been as filed (Rule 70.2(c)):
		(Any replacement she report.)	eet contail	ning such	amendments must be referred to under item 1 and annexed to this
6.	Add	itional observations, if	necessar	y:	
V.		soned statement und tions and explanation			rith regard to novelty, inventive step or industrial applicability; ch statement
1.	Stat	ement			
	Nov	elty (N)	Yes: No:	Claims Claims	1-13
	Inve	ntive step (IS)	Yes: No:	Claims Claims	1-13
	Indu	strial applicability (IA)	Yes: No:	Claims Claims	1-13

2. Citations and explanations see separate sheet

#### VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made: see separate sheet



#### INTERNATIONAL PRELIMINARY International application No. PCT/ZA00/00024 **EXAMINATION REPORT - SEPARATE SHEET**

Due to the specific process steps and parameters the claimed process for the production of 1. furfural is considered to be novel vis-à-vis the state of the art as represented by the documents cited in the International Search Report.

Vis-à-vis this state of the art an inventive step can be acknowledged since, for the process claimed, the parameters and conditions as well as its yield in the order of 100% have not been obvious to a person skilled in the art.

2. The use of the terms "a... predetermined temperature" and "a gradual reduction of pressure" in Claim 1 without further definitive qualification therein renders this claim obscure in scope in that it does not indicate any specific values. The claims shall define the matter for which protection is sought and therefore the meaning of the terms of a claim should, as far as possible, be clear for the person skilled in the art and not throw doubt on the extent of protection (Article 6 PCT). However, the amendments to Claim 1 as proposed in Applicant's letter dated 13/03/01 could be regarded as sufficiently clear in defining the terms objected to.

#### FOR THE PURPOSES OF INFORMATION ONLY

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#### PROCESS FOR THE MANUFACTURE OF FURFURAL

#### TECHNICAL FIELD OF THE INVENTION

This invention relates to a process for the manufacture of furfural.

#### **BACKGROUND OF THE INVENTION**

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Chemical reactors must be designed to suit the characteristics of the process intended. In making furfural, this has not been the case. For the first industrial production of furfural, QUAKER OATS used reactors from an abandoned cereal process as they happened to be available, and such reactors have been used ever since. Later, ROSENLEW and ESCHER WYSS built furfural plants based on reactors designed for making wood pulp. None of the industrial furfural reactors employed today were conceived to meet the special requirements of furfural production, and it is, therefore, not surprising that the yields obtained with these reactors do not even exceed 60%.

The principal yield losses are caused by a reaction between furfural and xylose, so that striving for a high yield forbids having furfural and xylose in the same place. All existing furfural reactors violate this requirement. By pointedly eliminating this deficiency, the process here described permits attaining yields in the order of 100%.

In analytical chemistry, the conversion of pentosan or pentose to furfural is used for a quantitative determination of these substances. This is possible as it was shown that in this procedure the furfural yield is a proven 100%. The procedure consists in an atmospheric digestion of pentosan or pentose in 12% aqueous HCl saturated with NaCl. By contrast, in the present industrial furfural processes mentioned above, a pressure reactor is used to submit the raw material to a steam treatment. By condensing, the steam effects heating to a constant temperature, and by passing through the raw material, it entrains furfural produced therefrom. The furfural reaction is catalysed either by added mineral acid or by various carboxylic acids (mainly acetic acid and formic acid) formed from the raw material. As compared to the analytical furfural process, a fundamental difference lies in the fact that in the latter process an appropriate heat input maintains the reaction medium in

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-2-

a state of boiling, whereas in the industrial processes at any pressure a condensation of steam is thermodynamically incapable of bringing the reaction medium, a pentose solution. to boiling, because of the boiling point elevation caused by the xylose. The difference is illustrated schematically in Figure 1 showing phase diagrams for furfural in an aqueous solution boiling at  $110^{\circ}$ C (12% HCl saturated with NaCl), and in an aqueous solution boiling at  $101^{\circ}$ C (xylose solution). If a small furfural concentration  $\xi$  is generated in the first system representing the analytical furfural process, this leads to point A lying in the vapour field, which means that any furfural formed in this boiling solution will be instantly transformed to vapour where it cannot react with pentose as the latter is not volatile. Consequently, in this case, loss reactions between furfural and pentose are impossible, which explains the proven yield of 100%.

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On the other hand, if a small furfural concentration  $\xi$  is generated in the second system, and if this system is heated by condensing steam at atmospheric pressure, this leads to point B lying in the liquid field. Hence, in the present industrial furfural reactors the reaction medium is not brought to boiling, so that the furfural remaining in solution can react with pentose to form furfural pentose, which explains the known high yield losses. The entrainment of furfural vapour by the steam flow does not change this statement to any significant extent, since this entrainment is a slow and inefficient process giving the loss reactions in the liquid phase plenty of time to take place.

As the principal difference between the analytical furfural process of 100% yield and the industrial processes of less than 60% yield lies in the fact that in the first case the reaction medium is boiling while in the second case it is not boiling, it was compelling to create an industrial process in which the reaction medium is maintaining in a state of boiling. In view of the fact that with giant furfural reactors, charged with solids not conductive to being stirred, an indirect energy input by heating the walls can be ruled out, it is the essence of this invention to bring about continuous boiling by a gradual (slow) depressurisation. In this fashion, a uniform boiling down to molecular dimensions is enforced without a need for mixing.

Apart from the poor yields achieved, the present commercial processes available are extremely expensive to operate. This is due to the large quantities of steam required.

typically 30 to 50 tons of steam per ton of furfural produced, and also the lengthy reaction times of between 2 and 5 hours.

It is therefore an object of this invention to provide a manufacturing process which not only produces a greater yield, but also requires a lower input of steam per ton of furfural produced and results in a shorter reaction time.

#### DISCLOSURE OF THE INVENTION

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According to the invention, a process for the manufacture of furfural includes the steps of charging a reactor with a pentosan containing material, acidified or not, heating the charge by introduction of pressurised steam to a first predetermined temperature, closing the steam inlet valve of the reactor and subjecting the charge to a gradual reduction of pressure until a second predetermined temperature is attained, the depressurisation maintaining the liquid phase within the reactor in a constantly boiling state.

In the preferred form rate of depressurisation is sufficient to complete the conversion to furfural before a second predetermined temperature is attained. Also in the preferred form of the invention, the charge is acidified prior to heating.

Also in the preferred form of the invention, the gradual depressurisation comprises the controlled leaking of a stream of vapour from the reactor until the second predetermined temperature is attained.

In one form of the invention, a first depressurisation is followed by a reheating to a temperature at or near the first predetermined temperature, the reheating being followed by a second gradual depressurisation.

Subsequent reheating and depressurisation cycles may also be employed if required.

In one form, steam may be added during depressurisation to increase the reaction temperature and improve yield.

In the preferred form of the invention, the charge material may be in solid or liquid form. Bagasse from sugar cane is a common feed and may be added to the reactor in solid or slurry form. Alternative feeds may include any other pentose-containing material, typical examples being corn cobs, bamboo, wood chips, olive press-cake amongst others.

Also in the preferred form of the invention the gradual depressurisation takes place in the temperature range between 280° Celsius and 150° Celsius, however the preferred range of operation is between 230° Celsius and 170° Celsius.

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By an appropriate choice of the first and second temperatures, and by appropriate selection of a mineral or organic acid concentration, it is possible, if desired, to complete the process in a single depressurisation period since high temperatures and high acidity result in a short reaction time.

In the preferred form of the invention, phosphoric acid is used as the catalyst.

An apparatus for use in a process according to the invention comprises a pressure reactor including an inlet for steam under pressure, and an outlet for condensate vapour, the inlet and outlet including one or more valves for controlling the flow rate therethrough.

The outlet includes, after a valve, an orifice plate of predetermined dimensions for assisting in controlling the rate of depressurisation. In this form, the valve and orifice plate may be operated in tandem to obtain a range of depressurisation rates or a flow control valve governed by temperature or pressure can be used.

In any form of the invention the reactor may be thermally well insulated.

In an alternative form of the invention the reactor walls are designed to be heated. Also in this form, all valve operations are preferably controlled automatically by a computerised control unit. It has been demonstrated experimentally, on a pilot plant scale, that by maintaining the liquid phase of the reaction medium in a state of boiling throughout the reaction period, the furfural yield obtained is substantially greater than current

commercial processes, and if correctly controlled may approach yields achieved in the analytical furfural process. The Applicant contends further that apart from increasing the yield, the process of the invention is operable at substantially lowered capital and productions costs, for the following reasons:

- (1), The process of the invention does not use steam for stripping furfural from the mass of feed material as once the reactor is sufficiently heated, the steam inlet is closed. Further steam will only be required briefly if a reheating cycle is employed.
- (2), As a result of the non-use of steam to strip the furfural, the volume of condensate existing the reactor is significantly reduced and the concentration of furfural therein will be proportionately increased in relation to existing processes. This increased furfural concentration will greatly simplify the primary azeotropic distillation. In special cases, for instance in the application of the furfural as a nematicide, no distillation is needed at all.
- (3), The product of the invention contains less acetic and formic acid (formed from the raw material) since, after reaching the second predetermined temperature of the decompression, most of these by-products are discharged with the residue. This greatly reduces the loading of the effluent generated by the plant.

#### **DESCRIPTION OF THE INVENTION**

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The process according to the invention is described below with reference to Figure 2 which is a schematic diagram of the process and apparatus.

A thermally well insulated reactor 1 charged with raw material acidified or not, is heated to a temperature  $T_1$  by admitting steam through valve 2 while the valves 3 and 4 are closed. During the very short heating process, the steam condenses, thus increasing the moisture content of the charge. Then, valve 2 is closed and a leak valve 3 is opened so as to produce a steady small flow of product vapour by gradual depressurisation. This causes a slow drop in temperature. When in this fashion a suitably chosen temperature  $T_2$  is reached, the leak valve 3 is closed to terminate the first "gradual depressurisation". If at the end of this period no more furfural was obtained, the digestion is completed by opening

valve 4 to discharge the residue. If, however, furfural was still obtained, the reactor is reheated and submitted to another "gradual depressurisation" period. This procedure can be arbitrarily repeated. All valve operations are governed by an automatic control unit 5.

By an appropriate choice of the temperatures  $T_1$  and  $T_2$ , and by an appropriate choice of the acid concentration, it is possible, if desired, to complete the process in a single depressurisation period since high temperature and high acidity permit a short reaction time.

Needless to say, designing such an operation is complicated as the furfural reaction takes place over a wide range of temperatures (e.g. from 230°C to 160°C), but once calculated, the practical realisation of the process is extremely simple.

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As due to the continuous leak stream the reaction medium is maintained in a state of boiling throughout the reaction period, the furfural yield corresponds to that of the analytical furfural processes by lying in the order of 100%.

#### **CLAIMS:**

1. A process for the manufacture of furfural characterised in that the steps of charging a reactor with pentosan containing material, heating the charge by introduction of pressurised steam to a first predetermined temperature closing the inlet valve of the reactor, and subjecting the charge to a gradual reduction of pressure until a second predetermined temperature is attained, the depressurisation being at a rate sufficient to maintain the liquid phase within the reactor in a constantly ebullient state.

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- 2. A process according to claim 1 characterised in that the charge is acidified prior to heating.
- 3. A process according to claim 1 characterised in that the rate of depressurisation is sufficient to complete conversion to furfural before the second predetermined temperature is reached.
- A process according to claim 1 characterised in that the complete conversion to furfural is obtained in more than one depressurisation from the first predetermined
   temperature to the second predetermined temperature by the addition of steam.
  - 5. A process according to claim 1 characterised in that steam is added during the depressurisation, for a predetermined period.
- A process according to claim 1 characterised in that the gradual depressurisation comprises the controlled leaking of a stream of vapour from the reaction until the second
   predetermined temperature is attained.

- 7. A process according to claim 1 characterised in that the gradual depressurisation takes place in the temperature range between 280° Celsius and 150° Celsius.
- 8. A process according to claim 7 characterised in that the temperature range of operation is between 230° Celsius and 170° Celsius.
- 5 9. A process according to claim 1 characterised in that phosphoric acid is used as the catalyst.
  - 10. A process according to claim 1 characterised in that acetic acid is used as the added catalyst.
- 11. An apparatus for the manufacture of furfural according to the process of claim 1 characterised in that it comprises a pressure reactor including an inlet for steam under pressure comprising one or more valves, and an outlet comprising a flow control valve or the combination of a shut-off valve and an orifice of predetermined dimensions.
  - 12. An apparatus according to claim 11 characterised in that the reactor is thermally well insulated.
- 15 13. An apparatus according to claim 12 characterised in that the wall of the reactor is adapted to be heated and/or heat exchange surfaces are incorporated inside the reactor.

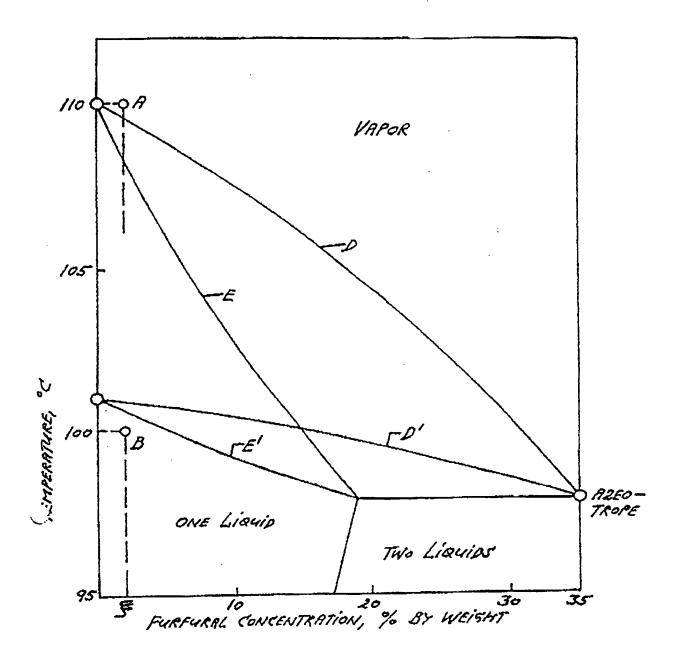


Figure 1. Phase diagram for explaining the difference between analytical and industrial furfural processes.

D and D': Dew point curves

E and E': Boiling point curves

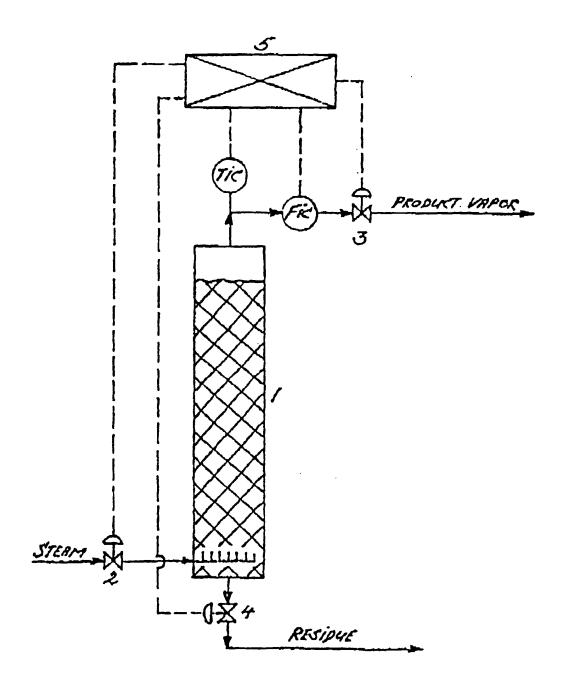


Figure 2 Schematic of the delayed decompression process for the production f furfural.

#### A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07D307/50 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC 7 CO7D Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Category ° Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. DE 31 39 188 C (H. KNAUTH) Α 1 - 1328 July 1983 (1983-07-28) claims 1,2 WO 81 00407 A (BERTIN & CIE.) 1-13 19 February 1981 (1981-02-19) claims 1-30 DE 38 42 825 A (FRIEDR. KRUPP GMBH) Α 1 - 1320 July 1989 (1989-07-20) claims 1-10 Α US 4 533 743 A (D. J. MEDEIROS, M. B. 1-6 BURNETT) 6 August 1985 (1985-08-06) claims 1-13 -/--Further documents are listed in the continuation of box C. χ X Patent family members are listed in annex. Special categories of cited documents : "T" later document published after the international filing date or priority date and not in conflict with the application but "A" document defining the general state of the art which is not considered to be of particular relevance cited to understand the principle or theory underlying the invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date "L" document which may throw doubts on priority claim(s) or involve an inventive step when the document is taken alone which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or other means ments, such combination being obvious to a person skilled document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report

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CPY - KVMI-R

DC - M24

FS - CPI

IC - C21B13/00 ; C22B1/00

IN - GLUSHAK A M; GUBIN G V; TSYURYUPA A D

MC - M24-A01A

PA - (KVMI-R) KRIV MINE ORE INST

PN - SU1225867 A 19860423 DW198648 003pp

PR - SU19843816523 19841121

XA - C1986-137742

XIC - C21B-013/00 ; C22B-001/00

- AB SU1225867 The process consists of loading the material, heating, reducing the material to magnetite with a solid and/or gaseous reducing agent and discharging the prod.
  - The firing process takes place until complete redn. to magnetite of the ore fraction of greater than 10mm is obtd. The final prod. of the firing, when it is discharged into the cooler, is treated with a gas-steam-air mixt. contg. 1-5% of O2.
  - ADVANTAGE The concn. of magnetite in the fired prod. obtd. from the redn. of lump iron-contq. materials is increased.
  - In an example, the degree of redn. to magnetite of the greater and less than 10mm fractions was 99 and 100% respectively. Bul.15/23.4.86 (3pp Dwg.No 0/0)
- IW REDUCE FIRE LUMP IRON CONTAIN MATERIAL COOLING FINAL PRODUCT GAS STEAM AIR MIXTURE
- IKW REDUCE FIRE LUMP IRON CONTAIN MATERIAL COOLING FINAL PRODUCT GAS STEAM AIR MIXTURE

INW - GLUSHAK A M; GUBIN G V; TSYURYUPA A D

NC - 001

OPD - 1984-11-21

ORD - 1986-04-23

PAW - (KVMI-R) KRIV MINE ORE INST

TI - Reducing-firing of lump iron-contg. materials - involves cooling of final prod. with gas-steam-air mixt.